

# POLYMER FILMS DEGRADATION AND BREAKDOWN IN HIGH VOLTAGE AC FIELDS

Konstantinos Theodosiou\* — Isidoros Vitellas\*\*  
— Ioannis Gialas\*— Dimosthenis P. Agoris\*\*\*

This paper examines the mechanism of electrical degradation and breakdown of polymeric insulating films as a sequence of electron injection by Fowler-Nordheim tunnelling, and macro-ion bond scission resulting in the creation of another macro-ion and a free radical. This is a thermo-fluctuational process which involves the action of the stretching force by the local electric field. Breakdown initiation starts when an electron following a Poole-Frenkel hopping mechanism, is accelerated in a hole with sufficiently large dimensions. Experiments were executed for measuring the breakdown AC voltage  $V_b$  and dielectric strength  $F_b$ , with voltage rising rate 3 kV/sec, in order to examine their relation with specimen thickness  $d$  and hence to derive a steady state breakdown criterion. An attempt of prediction of the polymer lifetime is also taking place.

**Key words:** polymer, degradation, conduction, tunnelling, micro-voids, macromolecules.

## 1 INTRODUCTION

Polymeric insulating materials are used in solid insulations of high voltage equipment such as cables, insulators, transformers and electrical machines. In many applications polyethylene and its co-products are used as the main insulating material, because they have fine dielectric properties and a low production cost. In practice, the insulating materials may be arranged in one or more layers in the insulation and usually some additives are mixed with them for improving the insulation characteristics.

Many models have been introduced by researchers [1, 4, 7, 14] attempting to explain, macroscopically or microscopically, the aforementioned properties and characteristics. More recent researches consider electrical breakdown initiation as a molecular scale process, which is not the case in the classical approach. The free volume theory [5, 6, 7], which is an extreme value theory, predicts that breakdown starts when an electron having been accelerated in the longest free path, gains sufficient kinetic energy to hop over a potential barrier.

The objective of this paper is to focus on the AC field conduction and breakdown mechanism on polymeric insulation, studying experimental results of breakdown measurements on insulating films, with PET as the main insulating material. In the next section a brief overview of the theory of degradation and breakdown in polymers is employed.

## 2 BRIEF REVIEW OF THE ELECTRICAL CONDUCTION AND BREAKDOWN MECHANISMS IN POLYMERIC INSULATORS

Many papers published in the area have shown that especially in high fields the shape of the conduction is filamentary and starts with the electron injection from the metal electrode to the polymer [8, 9, 10]. This process is through the Fowler-Nordheim tunneling and allows electrons to overcome the potential barrier that exists between the metal electrode and the polymer. They have also noted that the formation of the so-called low density region [13, 16, 17, 18, 19] is the first step in the breakdown of solid insulators. This process is more likely to increase near the injecting electrode where the concentration of injected electrons is higher and the low density region expands first linearly and later in a more complex manner forming branches [13, 14, 15] and tree-like structures.

Once the low density region has been formed and under appropriate conditions [7] (mean free path, ionization energy  $E_i$  of the radicals and applied electric field  $F$ ), impact ionization may follow and the avalanche may propagate creating conduction channels. This finally leads to an increase in carrier multiplication that extends the channels and destroys the material inside them [11, 13].

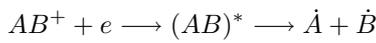
Electrons have been injected in the polymer, quickly become trapped after a few scatterings [11] because of the small mean free path and consequently form a negatively homo-space charge in the surface near to the injection contact. This trapping process takes place in localized energy states that exist in plenty in the poly-

\*University of the Aegean, 82100 Chios, Greece, E-mail: k.theodosiou@physics.org

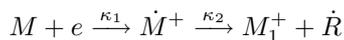
\*\*Public Power Corporation, 9 Leontarion Street, Kantza, 15351, Athens, Greece

\*\*\*University of Patras, 26500 Rio, Patras, Greece

mer due to many reasons such as structural or chemical imperfections etc. This homo-space charge creates an internal electric field opposite to the applied field that retards and may stop the injection process. According to Liu and Kao [10], in addition to the creation of the homo-space charge region, the trapping process results in energy transfer from the trapped electrons with two possible ways: (a) directly to the region around the trap causing structural damage breaking bonds like carbon-carbon or carbon-hydrogen (aging) and (b) to another electron and making it hot due to an Auger type process [11]. This electron can also cause structural damage and (or) create another hot electron. The process may continue and produce more radicals that form the low density region. Unfortunately this multi-stage process has some insuperable difficulties. In Ref. [20], this process is not regarded as a realistic model that describes the dissociation of macromolecules under the action of the electric field. The reasons are mainly the lack of any calculation about the probability of energy transfer or dissipation in each stage, the fact that the energy that is released in a trapping event 1.5 eV is lower than the energy for the C-C bond rupture 3 eV and the absence of any experimental results that indicate chain energy reactions in polymers. The authors of [20] consider that the model of Ref. [12] in which dissociation of macromolecules is a consequence of charge recombination according to the schematic mechanism



where  $AB^+$  is the macro-ion and  $(AB)^*$  the excited macromolecule, is more realistic. The reason is that the released energy 6 eV is higher than the C-C bond rupture energy. They also propose a model in which electrical degradation and breakdown occur due to ionization of macromolecules by electron tunnelling followed by thermo-fluctuational rupture of bonds according to the scheme



Unfortunately, they do not consider the influence of space-charge and image force potentials that is very important especially near to the electrode.

According to [7, 13, 14] electrical breakdown must at least begin at a molecular level and involve molecular scale processes, which is not part of the classical approaches. Because of the fact that the bulk of any semicrystalline polymer, such as polyethylene terephthalate (PET), contains crystalline and amorphous regions [2, 3] with the latter having a random structure, their volume is not completely occupied by atoms and includes empty spaces (free volume) which represent at least 2.5% of the total volume. These spaces differ from the crystal structure defects and are always present in the bulk in the form of empty holes between atoms. They are the reason of the density decrease and specific volume increase and show the inefficiency of molecular packing of the specific material. The hole size is of the order of the molecular size but because it is a random number, it can reach the order of a few nm ( $< 3 \times 10^{-9}$  m) [1]. Voids and micro-voids are

formed during manufacture by evaporation of decomposition products in various chemical reactions taking place in cross-linking, or by impurities and additives decomposition or by migration. Inside the hole, free electrons follow a free path significantly larger than that in the compact structure. They can gain a larger kinetic energy and, thus, lower the potential barrier  $E_\mu$  that try to overcome. The larger the free path and the hole volume, the more kinetic energy they gain [5, 6, 13]. In case the electrons acquire kinetic energy equal or larger than  $(E_\mu)$ , they overcome the barrier and the breakdown starts.  $E_\mu$  is not necessarily the ionization energy as it was originally supposed to be [7], but the energy of the potential barriers in the compact structure because electronic conduction is thermally assisted. Kao in [10, 11] had concluded that thermal energy is gained by an internal process via an Auger type phenomenon, while in Ref. [20] such a process is regarded to have a very low probability to happen. Some of the previously mentioned references will be discussed later in more detail.

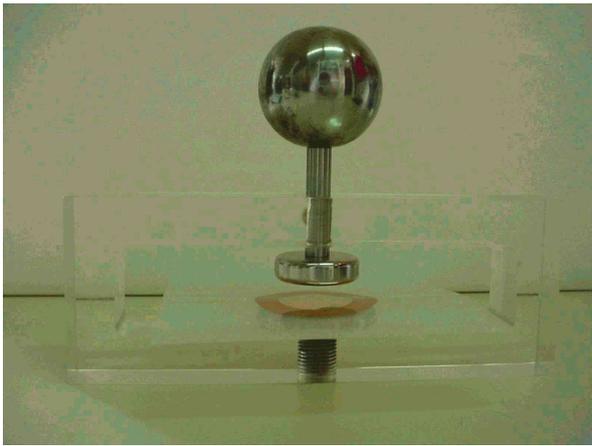
In the following section the description of the samples and the experimental procedure is presented. Then the experimental results and theoretical relations are discussed. Finally, a few concluding remarks are presented.

### 3 EXPERIMENTAL PROCEDURE AND SAMPLES

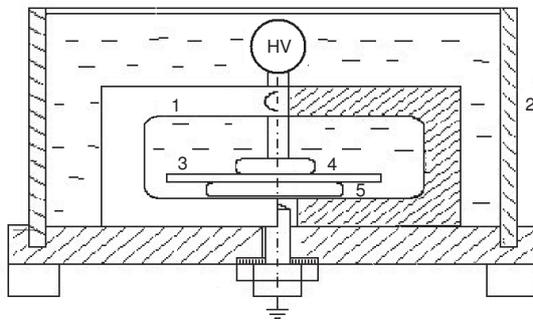
Polymer sheets are commonly used for the insulation of electric motor winding. The scope was the experimental determination of dielectric characteristics of such insulating materials, especially their relation with the thickness of the insulating material.

Specimens of high tenacity PET films with thickness of 23, 50, 75, 125, 190 and 350  $\mu\text{m}$  and in square form with dimensions  $120 \times 120 \text{ mm}^2$  were constructed. To ensure a good contact between specimen and test cell electrodes, additional copper electrodes were embodied on the surfaces of the specimen, with diameters 10 and 30 mm for breakdown measurements, and 45, 45 mm for PD measurements. These electrodes were constructed in vacuum conditions with instant evaporation of a suitable amount of copper, avoiding air enclosure between the samples surface and electrodes. Because of the short time duration of the copper evaporation, no damage occurred on the specimen surfaces, while a good contact was maintained between specimen and evaporated electrodes, as verified by systematic sampling in samples cross sections with the aid of a microscope. In Fig. 1 a specimen is shown.

A special experimental test cell was used, filled with power transformer oil and equipped with stainless steel electrodes with rounding edges, as shown in Fig. 2. The diameters of the main electrodes were equal to the corresponding copper electrodes of the samples. The procedure for putting a sample in the test cell was the following: the



**Fig. 1.** View of the specimen inside the experimental cell.



**Fig. 2.** Experimental cell filled with power transformer's oil. 1) Inner cell and electrodes base 2) Oil can 3) PET film sample 4) High voltage electrode 5) Earth electrode

electrodes base (1) was taken out of the test cell, the electrodes surfaces (4-5) were cleaned from the oil, the sample (3) was placed and fixed between the main electrodes and finally the base (1) was assembled in the bottom of the test cell and connected to an AC power supply. The dielectric strength of the oil (higher than 60 kV/mm) was measured regularly and was replaced when it was necessary.

### 3.1 Breakdown voltage measurements

The power supply used for the experiment was an AC 50 Hz, 100 kV, 100 mA. The voltage applied to the specimen increased from zero at a constant rate of 3 kV/s, to the breakdown voltage. When breakdown occurred, the voltage supply was interrupted automatically, with the current limiting protection system adjusted at 6 mA. The breakdown voltage was monitored using a digital voltmeter with memory and the maximum value in each specimen was recorded. For six groups of specimens, each one consisting of twenty samples with the same thickness  $y$ , the breakdown voltage  $V_b$  was measured and the dielectric strength  $F_b$  of each sample was calculated.

## 4 RESULTS AND DISCUSSION

### 4.1 Electrical degradation

#### 4.1.1 Fowler-Nordheim tunnelling in the electrode-polymer interface

As previously stated, the first step for the creation of the low-density region is the electron tunneling from the electrode metal to the bulk of the polymer. In high electric fields, ionization of macromolecules can occur due to the tunneling of electrons through reduced potential barriers (field ionization) as have been stated in many studies [7, 10, 25, 26]. The resulting current density due to Fowler-Nordheim tunneling is

$$J(t) = CF_l^2(t) \exp(-\beta/F_l(t)) \quad (1)$$

with

$$C = \frac{e^3}{16\pi^2\hbar\Phi_e}, \quad \beta = \frac{4(2m_e)^{1/2}}{3\hbar e}(\Phi_e)^{3/2} \quad (2)$$

where  $e$  and  $m_e$  are the charge and the effective mass of electron respectively,  $\hbar$  is the Planck constant,  $\Phi_e$  is the effective potential barrier in eV, and  $F_l(t)$  is the intensity of the local electric field acting in the contact, which will be discussed later.

The effective potential barrier through which electrons tunnel is actually the result of other potentials that sum up as follows:

$$\Phi_e = \Phi_m - \chi - P - \left[ \frac{e^3 F_l(t)}{4\pi\epsilon\epsilon_0} \right]^{1/2} - \frac{e^2}{4\pi\epsilon\epsilon_0 x} \quad (3)$$

with

$$\Phi_{ep} = \Phi_m - \chi \quad (4)$$

the potential in the electrode-polymer contact where  $\Phi_m$  is the metal work function and  $\chi$  the electron affinity of the polymer,

$$\Delta\Phi_{(t)} = \left[ \frac{e^3 F_l(t)}{4\pi\epsilon\epsilon_0} \right]^{1/2} \quad (5)$$

is the image force potential ( $\epsilon$  the dielectric permittivity of the polymer,  $\epsilon_0 = 8.85 \times 10^{-12}$  F/m the permittivity constant of the free space),  $P$  is the polarization energy produced by a pair of charges and the last term in (3) is the potential  $\Phi_n$  of the surrounding nuclei. The electron energy gained from the field is

$$W_e = eF_l(t)x \quad (6)$$

and hence the electrode-polymer barrier transparency (probability of overcoming the barrier) is equal to

$$D_e \cong \exp\left[-\frac{2\sqrt{2m_e}}{\hbar} \int_0^{x_0} (\Phi_e - W_e)^{1/2} dx\right], \quad (7)$$

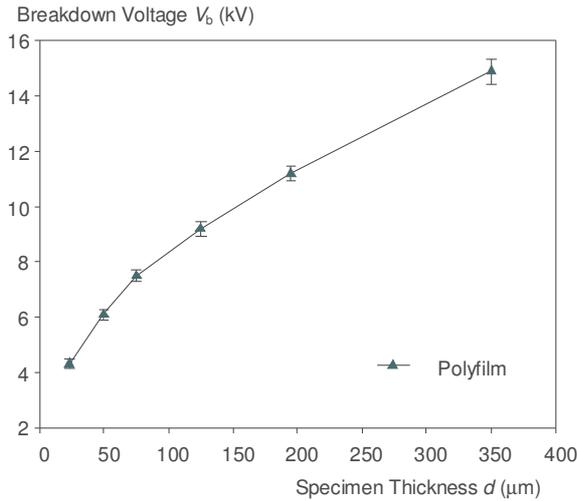


Fig. 3. Breakdown Voltage in PET film sample versus Thickness  $d$ .

where  $x_0$  is the barrier width, and if we assume a triangular shape, becomes

$$D_e \cong \exp\left[\frac{4(2m_e)^{1/2}(\Phi_e - W_e)^{3/2}}{3\hbar e F_l(t)}\right]. \quad (8)$$

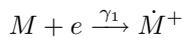
If we need to know the probability that electron tunneling has to cause macromolecule ionization, equation (3) should be rewritten as

$$\Phi_{ei} = I_g - P - \left[\frac{e^3 F_l(t)}{4\pi\epsilon\epsilon_0}\right]^{1/2} - \frac{e^2}{4\pi\epsilon\epsilon_0 x} \quad (9)$$

where  $I_g$  is the ionization energy of a macromolecule in the gaseous phase. The resulting tunneling frequency (tunneling probability per unit time) is given by

$$\gamma_1 = \nu_0 D_i \quad (10)$$

where  $\nu_0 \approx 10^{-16}$  Hz is the electron collision frequency with the barrier. The last two equations give an estimation for the tunneling macromolecule ionization rate that can be described by the following schematic mechanism



where  $M$  macromolecule and  $\dot{M}^+$  the resulting macroion.

At this point it is necessary to elucidate the role of the electric field acting in a specific micro-region. The local electric field  $F_l(t)$  is

$$F_l(t) = \alpha \frac{V}{d} - F_i(t) \quad (11)$$

where  $V$  is the applied voltage,  $d$  is the polymer thickness (electrode spacing),  $\alpha$  the local over-stress factor which depends on the local morphology and  $F_i(t)$  the internal electric field created by the trapped electrons. This field tends to retard the on-coming groups of injected electrons and its intensity is given by

$$F_i(t) = \frac{Q(t)}{\epsilon\epsilon_0} \left(1 - \frac{x_0}{d}\right) \quad (12)$$

with  $Q(t)$  the total trapped charge per unit area and  $x_0$  the position of its center in the specimen. If we consider the expression of electron trapping rate [10], the total trapped charge will be then

$$Q(t) = ex_0 N_t \left[1 - \exp\left(-\frac{\sigma}{e} \int_0^t J(t) dt\right)\right]. \quad (13)$$

Now the variation of the intensity of the local electric field can be evaluated by differentiating relation (11)

$$\frac{dF_l(t)}{dt} = (\alpha/d) \frac{dV(t)}{dt} - \frac{dF_i(t)}{dt}. \quad (14)$$

For an applied voltage with rising rate ( $\lambda kV/s$ ), the former relation gives

$$\frac{dF_l(t)}{dt} = \rho_a - \rho_i \quad (15)$$

with

$$\rho_a = (\alpha/d)\lambda \quad (16)$$

and (because of the fact that  $x_0 \ll d$  and by differentiating relation (13))

$$\rho_i = \frac{eN_t}{\epsilon\epsilon_0} \left\{ \left[ \frac{\sigma J(t)d}{e} + \frac{dx_0}{dt} \right] \exp\left(-\frac{\sigma}{q} \int_0^t J(t) dt\right) - \frac{dx_0}{dt} \right\}. \quad (17)$$

It is obvious from (17) that  $\rho_i$  is controlled by many parameters such as carrier mobility, distribution of traps and their capture cross section, dielectric permittivity etc. Especially for  $x_0$ , it can be said that is not a constant but moves towards the injection contact and is always negative when a DC voltage is applied. This happens because after the first group of injected carriers is trapped somewhere in the bulk, it forms the first distribution of space charge that tends to retard the next group of injected carriers. Gradually, the traps between the space charge center and the injection contact are filled in the same direction. It can be seen from (15) and (1) that there are three possible ways to describe the  $J - F_l$  or  $I - V$  relation.

- (i)  $\rho_a > \rho_i$  then  $F_l$  increases and consequently  $J$  also increases.
- (ii)  $\rho_a = \rho_i$  thus  $F_l$  becomes time independent and  $J$  becomes saturated, as a result of constant  $\rho_i$ .
- (iii)  $\rho_a < \rho_i$  and  $J$  after reaching a peak value, decreases with  $F_l$  increasing. This will happen if  $N_t$  or  $\sigma$  or both are large.

As it was stated above, as the first group of injected carriers is trapped somewhere in the bulk, it tends to retard the next group of injected carriers. As the applied field is increasing, the deep traps between the space charge center and the injection contact are filled and the further injection is enhanced. It is also very important to notice that each trapping event is associated with an energy of the order of 2 eV depending on the trap energy

level, but in any case not enough to directly rupture a C–C bond that needs more than 3 eV to do so. This energy can be also dissipated by creating thermal instability in the micro-region around the trap.

Another very important mechanism in AC fields that can directly lead to macromolecule dissociation, bond breaking and hence formation of low density region is charge recombination (a free electron and a positive macro-ion pair) [20]. The release of energy in this case is in the order of almost 6 eV and is accompanied by electroluminescence. Contrary to the above, charge recombination is not significant in the DC fields [22]. In the next sections we will discuss the aspects of the second part of the breakdown mechanism that leads to macro-ion dissociation.

#### 4.1.2 Macro-ion bond rupture

After the macromolecule ionization, macro-ions are subjected to the electric field which can induce mechanical strain, especially in the region near the electrode where the charge concentration is likely to be larger. In the the case of AC field, there will be a localized viscoelastic response of the macro-ion segments and a massaging in the field direction. The strains induced and the viscoelastic loss processes will favor bond rupture. The rupture energy  $G^+$  for a C–C bond in a macro-ion is of the order of  $\approx 1.9$  eV and is lower than the energy for breaking the same bond in the macromolecule  $G \approx 3.6$  eV [20, 21]. Due to the effect of the electric field,  $G^+$  decreases and becomes

$$G_F^+ = G^+ - l_0 e F_l \quad (18)$$

where  $l_0 \approx 1 \text{ \AA}$  is the activation length<sup>1</sup> and  $F_l$  the local electric field from equation (11). This significant decrease of the bond dissociation energy in the macro-ion makes its bonds favorable to scission through a thermofluctuational mechanism with a probability

$$P_{sc} = \exp\left(-\frac{G^+ - l_0 e F_l}{kT}\right). \quad (19)$$

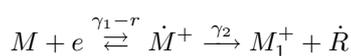
The macro-ion dissociation frequency is given by

$$\gamma_2 = \frac{1}{\tau_0} \exp\left(-\frac{G^+ - l_0 e F_l}{kT}\right) \quad (20)$$

where  $\tau_0 \cong 6.25 \times 10^{-12}$  s. As a result from the last equation, the probability of scission is increased dramatically when the local electric field approaches the value

$$F_l = \frac{G^+}{l_0 e}. \quad (21)$$

This value forms the maximum local electric field that the macro-ion bond can sustain, thus the criterion for bond scission. At this point the second stage of the polymer dissociation process can be added to the first one that described in Section 4.1 as follows



where  $M_1^+$  is a new macro-ion and  $\dot{R}$  a free radical. The last schematic process represents the degradation mechanism of a polymer and can be used for its lifetime prediction. When a sufficiently large amount of the bonds of the polymer is destroyed, breakdown is unavoidable. The left arrow and the factor  $r$  are added to stress the role of charge recombination in the AC voltage, emphasizing the fact that although it dispossess carries, provides a large amount of energy that can also cause bond rupture as it has been previously stated. Although an analytical solution is very difficult to be found due to time variation of  $\gamma_1$  and  $\gamma_2$ , for room temperatures and electric fields that are not approaching very much breakdown, the lifetime  $\tau_{pl}$  of the polymer its undoubtedly depends upon the electric field strength with an exponential relation. As the  $F_l$  increases,  $\tau_{pl}$  decreases. Many researchers have concluded in this result [7, 20, 30].

#### 4.2 Breakdown initiation by electron hopping and Poole-Frenkel mechanism

As it was stated above, PET is a partially crystalline insulating material with a large band gap. The movement of electrons in the bulk occurs via hopping between localized states-traps below the conduction band, in which the hopping probability is increased by the electric field, due to Poole-Frenkel effect. It must be stated here that the hopping process for sort time breakdown experiments, is taking place between shallow traps located in the region of 0.3–0.6 eV [14, 20]. They may be foreign molecules, carbonyl or other more complex groups, or even polarized states and their concentration ( $10^{18} \text{ cm}^{-3}$ ) is sufficiently larger than that of the deep traps [1, 14]. At high electric fields the traps depth is reduced as a result of Poole-Frenkel mechanism and the current is increased exponentially with the square root of the electric field [24]. Under these conditions, electrons velocity  $u_{th}$  and concentration  $n_e$  increase supra-linearly [7, 23, 27, 31]. They both depend on the ionization energy  $I_g$ , temperature  $T$  and the electric field strength  $F_l$  that lowers the potential barrier. According to the Poole-Frenkel model [27], the following approximation can be derived for these two quantities:

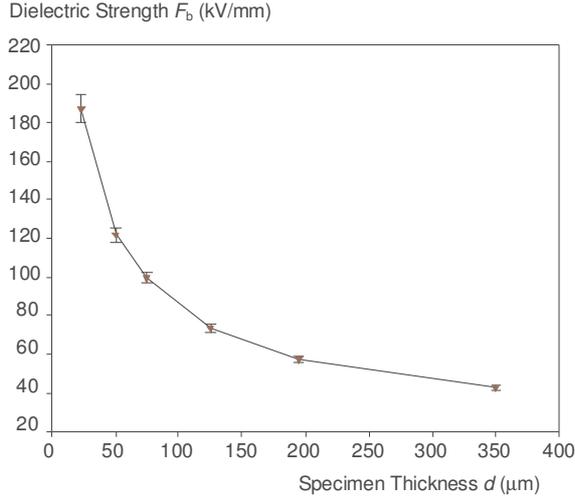
$$u_{th} = \nu x \exp[-(I_g - e F_l x)/kT], \quad (22)$$

$$n_e \simeq N_e \exp[-(I_g - \beta_{PF} F_l^{1/2})/(2kT)] \quad (23)$$

where  $N_e$  is the ionized center concentration,  $\beta_{PF} = [e^3/(\pi\epsilon_0\epsilon)]^{1/2}$  is the Poole-Frenkel parameter with  $\epsilon_0\epsilon$  been the static permittivity. Electrons hop randomly over energy barriers and the velocity gained due to acceleration from the applied field is added to the thermal velocity. If the length of the free path inside a hole is  $x$ , the kinetic energy  $K$  gained by the electron, will be equal to:

$$K = eV = e F_l x. \quad (24)$$

<sup>1</sup>It must be stated here that activation length  $l_0$  can be changed by local thermal fluctuations



**Fig. 4.** Breakdown Electric field strength in PET film sample versus Thickness  $d$ .

The probability for an electron to overcome the energy barrier, is given by the Frenkel formula [27]:

$$P_\mu = \exp[-(I_g - eF_l x)/(kT)]. \quad (25)$$

Electrons are passing through a hole with an overall velocity (thermal and gained from the field)  $u_o$  of the order of  $10^5$  m/s in a time  $t = x/u_o \simeq \sqrt{[3]V_h}/u_o$  were  $V_h$  the hole volume. Thus the hole is crossed by  $n_e V_h/t \simeq 10^5 n_e V_h/x \simeq 10^5 n_e V_h^{2/3}$  electrons per second. This constant electron flow leads to a current density

$$i = n_e e u_o \quad (26)$$

which is insignificant in the case of not very high applied fields, mainly due to the continuous reduction of the electrons energy in every further step. At very high fields ( $\simeq 10^9$  Vm $^{-1}$ ) the energy gained from the field becomes large enough so the electrons have a large probability to overcome the barrier. Considering ( $P_\mu = 1$ ), we have:

$$F_l = I_g/e x. \quad (27)$$

From equations (24) and (25), it is obvious that the breakdown voltage  $F_b$  is inversely proportional to the free path  $x$ . Equation (27) is the criterion for breakdown initiation. If rearranged as:

$$F_l x = I_g/e = V_\mu \quad (28)$$

indicates that quantity  $V_\mu$  depends on the polymer structure thus on the size of the holes in it [7] and generally it is not constant. For a specific polymer,  $V_\mu$  depends on the temperature, the relative motion between the macromolecules and the mechanical stress.

The breakdown criterion shows that the longer the free path and the size of the hole, the lower the breakdown voltage. Breakdown process initiates from that hole with the longest free path. The free path is actually the diameter of the hole if we assume a spherical shape. The hole size is randomly distributed for a specific volume sample

of the material. As we are interested in the maximum (extreme) value of the free path and the hole with the maximum size in that sample, rather than in the average value, if we increase the volume of the sample, we actually increase the probability of having a bigger hole and a longer free path.

It has been found [3, 28] that the probability of having a hole with volume larger than  $V_h$ , is exponentially distributed:

$$P(V_h) = \exp[-(V_h/V_{h1})] \quad (29)$$

where  $V_{h1} = 1 - e^{-1} = 0.632$ , is the expected value. If we assume that hole has a spherical shape, the longest free path  $w$  is proportional to the cubic root of the biggest hole's volume. Similarly, the probability of having a free path larger than  $w$ , is:

$$P(w) = \exp[-(w/w_1)^3] \quad (30)$$

where  $w_1 = 1.443w_m$  and  $P(w_m) = 0.5$ . The third power in equation (30) is generally smaller because holes are oblong rather than spherical, so we can use  $k$  instead of 3 with  $1 < k \leq 3$ .

If we choose a hole from a sample of  $n$  holes, taking into account equation (30), we derive the following relation about the characteristic largest value  $x_n$ , of the free path:

$$x_n = w_1 (\ln n)^{1/3}. \quad (31)$$

If we increase the sample, we take a larger value for the free path:

$$x_N = x_n + a \ln n \quad (32)$$

where  $a$  is a function of  $\ln n$  [29]. The last relation clearly indicates that with the increase of the sample, the largest free path also increases.

If we assume that we have the area  $S$  of the electrode, the total volume of the specimen that is exposed under electric strength is  $V_t = Sd$ . If there are  $n$  holes in this volume, each one with a volume of  $V_h = cw_1^3$  the total volume  $nV_h$  of the holes, is a fraction  $\theta$  of the  $V_t$  (approximately 2.5%). Thus we take:

$$ncw_1^3 = \theta Sd \quad (33)$$

and then

$$x_n = [(\theta Sd \ln n)/(nc)]^{1/3}. \quad (34)$$

Substituting  $x_n$  in equation (27), we have

$$F_b = \frac{I_g}{e[(\theta Sd \ln n)/(nc)]^{1/3}}. \quad (35)$$

The latter relation can be expressed in a general form as

$$F_b \propto \kappa/(b + \ln d)^{1/k}. \quad (36)$$

( $n \propto d$ ) were  $\kappa$  and  $b$  are constants. The diagrams in Figs. 3 and 4, show results for six groups of specimens with different thickness. The error bars show the mean error of the mean value of each group of twenty specimens, calculated by the formula  $\bar{\sigma}_n = \sqrt{\frac{1}{n(n-1)} \sum_{i=1}^n (x_i - \bar{x})^2}$ .

Our percentage error values were between 2.1 minimum and 3.9 maximum. Equation (36) is consistent with the plot of our experimental results as it can be seen from these figures.

## 5 CONCLUSIONS

Electrical breakdown of polyethylene terephthalate (PET) films were measured under 50 Hz AC electric field. Electrical degradation and breakdown is a two-stage process. Electrons are injected from the electrode to the polymer by Fowler-Nordheim tunnelling in micro-regions that are favorable to enhance the injection due to lowering the barrier profile. These electrons may cause impact ionization of macromolecules transforming them to macro-ions. In the second stage, macro-ions are subjected to the electric field action and through a thermo-fluctuational mechanism, weakened carbon bonds are rupture causing structural damage (degradation) in the polymer. After the appropriate time, structural damage accumulation leads to the final breakdown. From the other hand intrinsic breakdown initiation, in constant temperature, may take place inside the hole with the longest free path, from an electron being accelerated by the electric field. The breakdown criterion indicates that dielectric strength is reciprocal to the longest free path and strongly related with the film thickness. The random nature of polymers indicates that the longest free path and hence the largest hole are more likely to exist in a thicker specimen that has a larger volume. Because the volume of insulation in reality is orders of magnitude larger than the specimen volume, it has to be noted that dielectric strength is much lower in this case. Another important fact is that in thicker films apart from bigger holes and voids, there are many regions (especially in the boundaries between amorphous and crystalline parts of the polymer) that can cause a local lack of homogeneity and hence a strengthening of the electric field.

## REFERENCES

- [1] DISSADO, L. A.—FOTHERGILL, J. C.: *Electrical Degradation and Breakdown in Polymers*, Peregrinus, London, 1992.
- [2] TOBOLSKY, A. V.: *Properties and Structure of Polymers*, Wiley, New York, 1960.
- [3] BUECHE, F.: *Physical Properties of Polymers*, Interscience, New York, 1962.
- [4] KAO, K. C.—HWANG, W.: *Electrical Transport in Solids*, Pergamon, Oxford, 1981.
- [5] ARTBAUER, J.: *J. Polym. Sci. C* **16** (1967), 447.
- [6] ARTBAUER, J.: *Kolloid Z. Z. Polym.* **225** (1968), 23.
- [7] ARTBAUER, J.: *J. Phys. D: Appl. Phys.* **29** (1995), 446.
- [8] KAO, K. C.: *IEEE Trans. Electr. Insul.* **EI-11** (1976), 121.
- [9] WATSON, D. B.—HEYES, W.—KAO, K. C.—CALDERWOOD, H. J.: *IEEE Trans. Electr. Insul.* **EI-1** (1965), 30.
- [10] LIU, D.—KAO, K. C.: *J. Appl. Phys.* **69** (1991), 2489.
- [11] KAO, K. C.: *Proc. Int. Conf. on Electrical Insulation (Canada)*, vol. 1, North-Holland/American Elsevier, Amsterdam, 1999, p. 517.
- [12] LEBEY, T.—LAURENT, C.: *J. Appl. Phys.* **68** (1990), 275.
- [13] FOSTER, E. O.: *J. Phys. D: Appl. Phys.* **23** (1990), 1506.
- [14] LEWIS, J. T.: *J. Phys. D: Appl. Phys.* **23** (1990), 1469.
- [15] DISSADO, A. L.—FOTHERGILL, C. J.—WISE, N.—WILLBY, A.—COOPER, J.: *J. Phys. D: Appl. Phys.* **33** (2000), L109.
- [16] KAO, K. C.—XE. H. K.—TU, D. M.: *J. Electrostatics* **16** (1984), 115.
- [17] XIE, K. H.—KAO, K. C.: *IEEE Trans. Electr. Insul.* **EI-20** (1986), 293.
- [18] SUEDA, H.—KAO, K. C.: *IEEE Trans. Electr. Insul.* **EI-17** (1982), 221.
- [19] BUDENSTEIN, P. P.: *IEEE Trans. Electr. Insul.* **EI-15** (1980), 225.
- [20] ZAKREVSKIY, V. A.—SUDAR, N. T.—ZAOPO, A.—DUBITSKY, Y. A.: *J. Appl. Phys.* **93** (2003), 2135.
- [21] AKLONIS, J. J.—McKNIGHT, W. J.: *Introduction to Polymer Viscoelasticity*, 1983.
- [22] BAMJI, S. S.—BULISKI, A. T.—DENSLEY, R. J.: *J. Appl. Phys.* **61** (1987), 694.
- [23] ADAMEC, V.—CALDERWOOD, H. J.: *J. Phys. D: Appl. Phys.* **8** (1975), 551.
- [24] PATSCH, R.: *J. Phys. D: Appl. Phys.* **23** (1990), 1497.
- [25] KOEHLER, M.—HUMMELGEN, I. A.: *J. Appl. Phys.* **87** (2000), 3074.
- [26] RAVINDRA, N. M.—ZHAO, J.: *Smart. Mater. Struct.* **1** (1992), 197.
- [27] FRENKEL, J. I.: *Phys. Rev.* **54** (1938), 647.  
*Kinetic Theory of Liquids*, Dover, New York, 1955.
- [28] COHEN, M. H.—TURNBULL, D.: *J. Chem. Phys.* **31** (1959), 1164.
- [29] GUMBEL, E. J.: *Statistical Theory of Extreme Values and Some Practical Application*, NBS, Washington, DC, 1954.  
*Statistics of Extremes*, Columbia University Press, New York, 1958.
- [30] DING, H. Z.—XING, X. S.—ZHU, H. S.: *J. Phys. D: Appl. Phys.* **27** (1994), 591.
- [31] FANJEAU, O.—MARY, D.—MALEC, D.: *J. Phys. D: Appl. Phys.* **33** (2000), L61.

Received 27 April 2004

**Konstantinos Theodosiou** is a lecturer in the Department of Financial and Management Engineering, University of the Aegean, Chios, Greece. He was born in 1967 in Greece and has obtained an MPhys, an MSc in Electronic Engineering and is working for a PhD in the field of electrical insulation. His research interests include degradation and breakdown of insulating materials, polymer physics, electromagnetics.

**Ioannis Gialas** is an Associate Professor in the Department of Financial and Management Engineering, University of the Aegean, Chios, Greece. He was born in 1960 in Greece and has obtained an MPhys, an MSc in Physics and a PhD in the field of Experimental High Energy Physics. His research interests are in the area of experimental high energy physics.

**Isidoros Vitellas** is Director of the High Voltage Laboratory in DEH (Public Power Corporation) Athens, Greece. He was born in 1954 in Greece and has obtained an Diploma in Electrical Engineering and a PhD in the same field. His research interests include electrical power generation and transfer, degradation and breakdown of insulating materials, electromagnetics.

**Dimosthenis Agoris** is an Associate Professor in the Department of Electrical Engineering and Computer Technology, University of Patras, Rio, Patras, Greece and Director of the High Voltage Laboratory in the same Department. He was born in 1952 in Greece and has obtained a Diploma in Electrical Engineering and a PhD in the same field. His research interests include electrostatics, electromagnetics, electrical power generation and transfer, degradation and breakdown of insulating materials.